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SYNTHESIS OF A SERIES OF ACETYLENE TERMINATED  
OLIGOMERS: STRUCTURE PROPER. (U) WRIGHT STATE UNIV  
DAYTON OHIO DEPT OF CHEMISTRY J J KANE MAR 84

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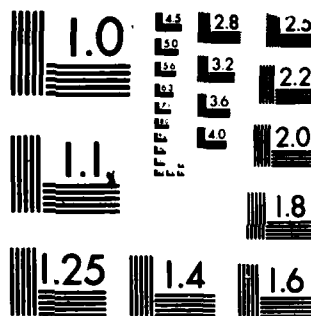
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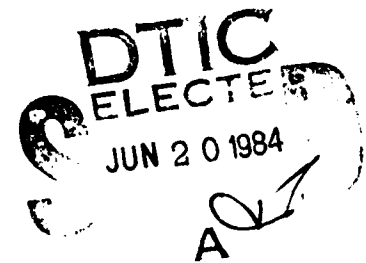
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Abstract

Key intermediates for the synthesis of a series of four bis-acetylene aryl ether sulfones have been synthesized. The intermediates are the oligomeric bis-phenols resulting from nucleophilic aromatic substitution of 4,4'-dichlorodiphenyl sulfone with an excess of the salts of each of the following bis-phenols: 2,2-di-(4-hydroxyphenyl)perfluoropropane (IV), 4,4'-dihydroxybenzophenone (V), 4,4'-dihydroxydiphenyl ether (VI), and 4,4'-dihydroxydiphenyl methane (VII).

Two of the resulting oligomeric bis-phenols (those arising from IV and VI) were converted to bis aryl bromides by the Ullman ether synthesis with excess amounts of m-dibromobenzene.

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Chief, Technical Information Division

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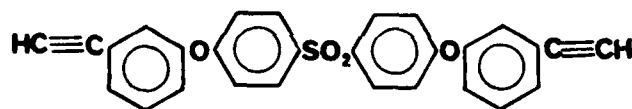


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## I. Introduction

Acetylene terminated (AT) oligomeric compounds have recently emerged as candidates to fulfill current needs for light weight structural composite materials in advanced aircraft and aerospace vehicles.<sup>1,2</sup> The AT compounds are addition curable, moisture resistant thermoset systems. Their cure chemistry is complex and results in a poly-ene cross-linked network.<sup>3</sup> Subsequent higher temperature cure reactions are believed to occur by cyclization reactions which are thought to form a variety of aromatic structures.

Recently, substantial effort has been directed<sup>4,5</sup> toward application of AT chemistry to provide materials for replacement of epoxy resins which are of limited use in matrix systems because they are moisture sensitive. Thus the AT compound 4,4'-di-(3-ethynyl phenoxy)-diphenylsulfone (ATS) exhibited acceptable after cure thermal properties, was insensitive to moisture



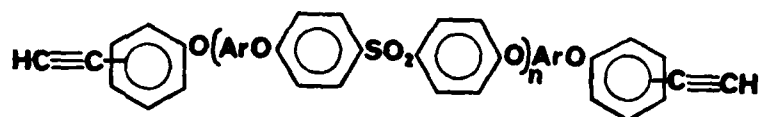
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and met all the processing criteria for a 350°F matrix material.<sup>6</sup> However, the cured material exhibited marginal values for energy to fracture and elongation to break which indicated that it was too brittle for end-use applications<sup>7</sup>.

It has been shown<sup>8</sup> in the AT-quinoxaline series that improved mechanical performance is achieved by increasing the molecular weight (or molecular length) between crosslink sites. However, as molecular weight between crosslinks increases processing parameters are also affected. Thus, a balance must be achieved between processing parameters of the oligomers ( $T_g$  and rheology) and intended use-temperature (350 F).

The syntheses and evaluation of thermal properties of a series of AT

arylether sulfone monomers and oligomers (represented by structure II) was recently summarized.<sup>5</sup>



II

The results confirm that most of the compounds which were included in the series cured to provide materials with Tg values above the minimum required for use at 350°F. This information also confirms that the acetylene terminated aryl ether sulfone structures are a fertile area for candidate compounds. Thus, in order to systematically evaluate structure-property relationships as a function of variations in the bis-phenol moiety in structure II, a synthesis and testing project was proposed and initiated. The state of progress of that project is the subject of this report.

## II. Discussion

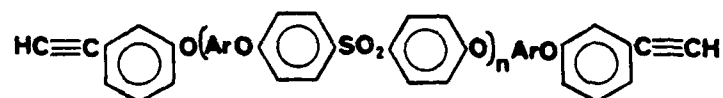
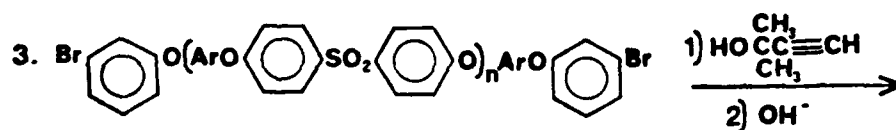
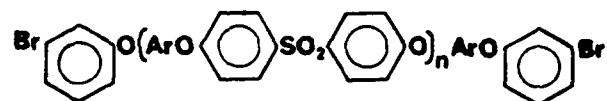
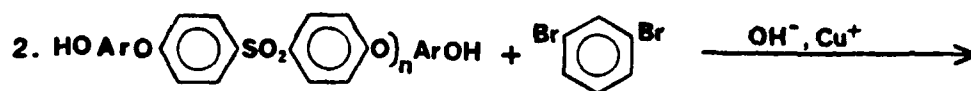
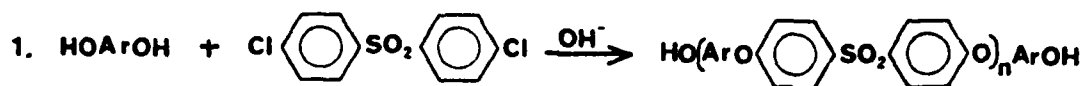
### A. Goals

The initial goals of this project included synthesis of a series of bis-acetylene terminated arylether sulfone monomers and oligomers, their cure, and thermal evaluation of the cured materials.

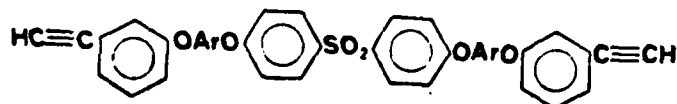
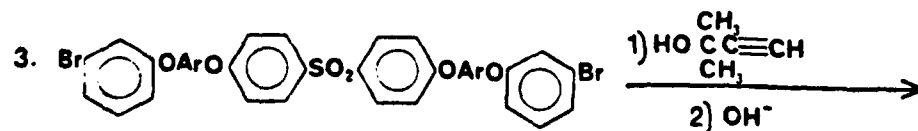
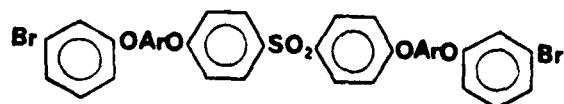
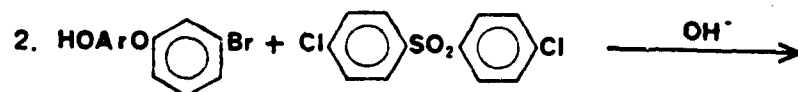
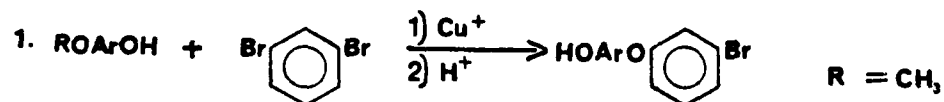
#### 1. Synthesis

The intended synthetic schemes are outlined below. Scheme A is aimed at synthesis of monomeric compounds (structure III,  $n = 1$ )

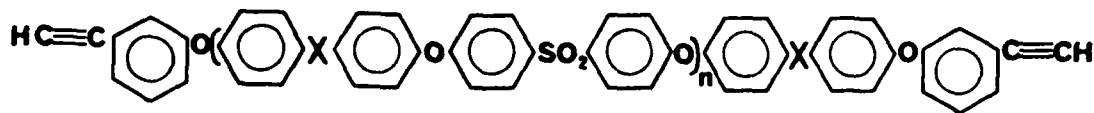
SCHEME B



SCHEME A



exclusively while Scheme B is directed at synthesis of a mixture of oligomers (Structure III,  $n = \text{one and larger}$ ). The bis-phenols included in



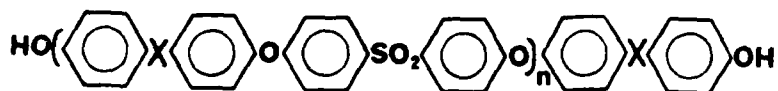
III

- a.  $X = C(CF_3)_2$
- b.  $X = C=O$
- c.  $X = O$
- d.  $X = CH_2$

this program are 2,2-di-(4-hydroxyphenyl)perfluoropropane (IV), 4,4'-dihydroxybenzophenone (V), 4,4'-dihydroxydiphenylether (VI) and 4,4'-dihydroxydiphenyl ether (VII) for synthesis of III a, b, c, and d respectively.

The syntheses outlined in Schemes A and B were organized as described below. Scheme B which is directed at preparation of the oligomeric materials involves the four reactions outlined below.

i. Reaction of the appropriate bis-phenol (IV, V, VI, and VII) with 4,4'-dichlorodiphenylsulfone to give the oligomeric bis-phenols (VIII a-d).

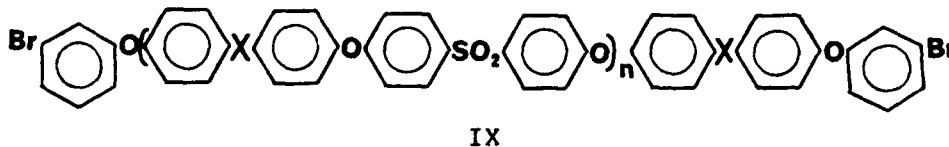


VIII

This reaction requires a four-fold excess of bis-phenol to insure phenolic end groups and relatively short chain lengths. It is usually done under inert, anhydrous conditions in refluxing N-methylpyrrolidone (NMP) and toluene with removal of by-product water. Reaction progress is monitored by following the disappearance of dichlorodiphenylsulfone

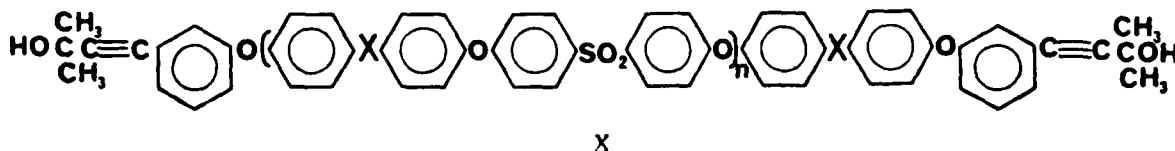
with TLC.

ii. Reaction of the oligomeric bis-phenols (VIII a-d) with m-dibromobenzene to give the oligomeric dibromo compounds (IX a-d).



This reaction is done in refluxing pyridine with  $K_2CO_3$  and CuI under anhydrous and inert conditions. Reaction progress is monitored by following disappearance of oligomeric bis-phenol reactants by TLC. A ten-fold excess of m-dibromobenzene is used to insure bromo end groups.

iii. Reaction of the oligomeric dibromides (IX) with 2-methyl-3-butyn-2-ol to give the oligomeric acetylene terminated acetone adduct (X).



This reaction is done in pyridine and triethylamine under anhydrous, inert conditions with the catalyst mixture, triphenylphosphine, di-(triphenylphosphine)palladium dichloride, and cuprous iodide.

iv. The final step involves thermal cleavage of the acetone adduct (X a,d) with KOH to give the desired acetylene terminated sulfone oligomers (III a-d). The work plan of the syntheses was to carry all of the bis-phenols (IV-VII) through each step outlined above before going on to the next step. Thus, all of the oligomeric bis-phenols (VIII a-d) were to be prepared before going on to preparation of any of the oligomeric dibromides (IX a-d).

## B. Results

In order to work out the details of each of the steps in the reac-

tion sequence, each step was practiced with bis-phenol-A, a cheap and readily available bis-phenol.

The following syntheses of Scheme B have been done.

1. The bisphenol 2,2-di(4-hydroxyphenyl)-perfluoropropane (V) has been converted to the oligomeric diol VIIa and then to the oligomeric dibromide IXa.

2. The bis-phenol 4-4'-dihydroxydiphenyl ether (VI) has been converted to the oligomeric bis-phenol (VIII c) and to the oligomeric (IX c).

3. The bis-phenol 4,4'-dihydroxydiphenylmethane (VII) has been converted to the oligomeric bisphenol (VIII d).

4. The bis-phenol 4,4'-dihydroxybenzophenone (V) has been converted to the oligomeric bisphenol VIII b.

#### IV. Experimental

##### 1. Reaction of 2,2-di(4-hydroxyphenyl)perfluoro propane (IV) with 4,4'-dichlorodiphenylsulfone.

Freshly sublimed IV (10.10 g, 30 mmol) and 2.15 g (7.5 mmol) of dichlorodiphenylsulfone was dissolved in a mixture of 75 mL toluene in a three necked round bottomed flask equipped with N<sub>2</sub> inlet, thermometer, stirring apparatus and reflux condenser with a Dean-Stark trap for water collection. After purging the mixture with N<sub>2</sub> for 30 min, 2.07g (15.0 mmol) of K<sub>2</sub>CO<sub>3</sub> were added. The reaction mixture was heated with stirring at reflux for 36 hours under N<sub>2</sub>. After cooling, the reaction mixture was added to a mixture of ice and excess HCl. The organic layer was separated from the aqueous acid with 300 mL CH<sub>2</sub>Cl<sub>2</sub>, washed with water, dilute HCl and then extracted with 300 mL 1% NaOH to remove unreacted IV. The organic layer was washed with water, dried with MgSO<sub>4</sub> and stripped of solvent to yield 4.48 g (66% yield) of VIII a, a

yellow oil.

2. Reaction of 4-4'-dihydroxybenzophenone (V) with 4,4'-dichlorodiphenylsulfone.

Bis-phenol (V), purchased from Pfaltz and Bauer was used without further purification. This reaction was done as in 1. above except that 21.2g (99.1 mmol) of V; 7.08 (24.6 mmol) of dichlorodiphenylsulfone and 6.81g (49.3 mmol) of  $K_2CO_3$  were used and the reaction mixture was heated at reflux for 45h.

3. Reaction of 4,4'-dihydroxydiphenylether (VI) with 4,4'-dichlorodiphenylsulfone.

This reaction was done as in 2 above using 21.68g (72.2 mmol) VI, 7.69 (26.8 mmol) dichlorodiphenylsulfone and 7.40g (53.6 mmol) of  $K_2CO_3$ . The solvent mixture was 100 mL NMP and 60 mL toluene. The reaction mixture was heated at reflux for 24 hours to yield, after workup, 9.03g (54.5% yield) of VIII c a yellow semi-solid.

4. Reaction of 4,4'-dihydroxydiphenylmethane (VII) and 4,4'-dichlorodiphenylsulfone.

This reaction was done in the same manner as 3 above using 19.31g (96.5 mmol) VII, 6.92 (24.1 mmol) dichlorodiphenylsulfone, and 6.66g (48.3 mmol)  $K_2CO_3$ . After workup, the reaction yielded 13.81 g (93.2% yield).

5. Reaction of m-Dibromobenzene with VIII a.

The oligomeric bis-phenol VIII a 4.48g (5.05 mmol) and 11.92g (50.5 mmole) of m-dibromobenzene were dissolved in 200 mL dry pyridine in a 3 necked, round bottomed flask equipped with thermometer, stirring apparatus and reflux condenser with a Dean-Stark trap. After flushing the mixture with  $N_2$  for 30 min, 3.49g (26.3 mmol) of  $K_2CO_3$  and 0.11g CuI were added and the mixture was heated at reflux with stirring (under  $N_2$ ) for 48h. After cooling to room tempera-

ture, the reaction mixture was filtered and poured into cold dilute HCl and allowed to stand overnight. The light brown oil which separated was taken up in  $\text{CH}_2\text{Cl}_2$ , separated and washed with water. The organic layer was dried over  $\text{MgSO}_4$  and stripped of solvent. Heating the residue at 110-120 C under vacuum removed the unreacted dibromobenzene and left 5.41g (89.6% yield) of crude 1Xa, a brown oil.

6. Reaction of m-dibromobenzene with VIII c.

This reaction was done as 5 above using 9.03 g (14.5 mmol) of the oligomeric bis-phenol VIII c, 34.5g (146 mmol) m-dibromobenzene, 10.1 (73 mmol)  $\text{K}_2\text{CO}_3$ , 0.33g CuI and 300 mL pyridine were used. The reaction mixture was refluxed for 36h.

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